Application of Waste Cooking Oil in Construction of Asphalt Pavement

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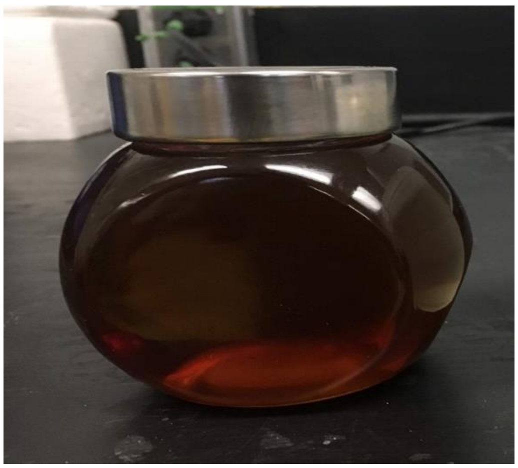

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The Harris Centre – MMSB Waste Management Applied Research Fund 2018-2019

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Executive Summary

Using reclaimed asphalt pavement (RAP) material in pavement construction is an environmentally friendly practice which economizes the pavement construction costs by replacing the virgin binder in the mix design. However, the asphalt available in recycled pavements is already oxidized and stiffened due to various environmental processes, which may accelerate the pavement distresses especially thermal cracking. To counteract this, rejuvenators are being used by reactivating and restoring the original properties of the neat asphalt binder. Waste Cooking Oil (WCO), identified as a waste material and pollutant for river and landfills, contains lighter oil components that are similar to asphalt, and is being used as a rejuvenator in this study. This research is designed to conduct a number of basic and advanced testing to investigate the effectiveness of WCO as a rejuvenator. The experimental program includes the determination of free fatty acid (FFA) contents in the WCO using GC-MS and later reduced these FFA contents by transesterification process which was denoted by treated WCO. Thin-Film Oven Test (TFOT) aged PG 58-28 binder was used as a control, followed by mixing rejuvenators at 3%, 6% and 9% by the weight of the total binder. To better and holistically evaluate the rheological properties, Dynamic Viscosity test was being carried out. And, the advanced test includes Fourier Transformed Infrared Spectroscopy (FTIR) for obtaining function group information. The experimental study found that with the improvement of WCO quality after treatment, the rejuvenation behavior of aged asphalt also increases significantly. The treatment of WCO changes the chemical composition of rejuvenated asphalt that exhibits better adhesion performance and rutting resistance compared to untreated WCO. From FTIR analysis, distinct peaks of C=O bond were found, and the peak intensity increased with the quality of WCO decreased, which is a clear indication of being the binder becomes softer. Based on the experimental analysis above, the treated WCO seemed to be effective in improving the rutting resistance with a better adhesive performance of binder and can be suggested as a potential rejuvenator for the construction of asphalt pavement.

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1. Introduction

In the pavement industry, using reclaimed asphalt pavement (RAP) material is a preferable method for enhancing environmental sustainability. Road agencies have been using RAP increasingly to reduce the burden on natural aggregate and to lower the disposal problems of reclaimed pavements. In addition, some new environmental regulations are contributing to making RAP materials more attractive to highway agencies. During its long-term service, the asphalt binder exposed to hot air and temperature, resulting in a change in their physical and rheological properties (*1*). Past studies show that the oxidized binder in RAP materials decreases the overall relaxation capacity of HMA and the binder exhibits more brittle nature that leads to the formation of cracks between the interface of aggregates and the binder (*2*). To address these problems, it is common to blend recycled asphalt with some recycling agents known as rejuvenator to reactivate its original property and to improve its fatigue performance (*3*). Generally, RAP materials consist of 4-6% of asphalt binder by weight of aggregate (*4*) and could reduce the cost of construction up to 34% for a range between 20-50% of using the RAP content (*5*).

Waste cooking oil (WCO), produced during cooking and frying activities, can be used as a good rejuvenator because it contains lighter oil fractions similar to asphalt. Every year, food markets generate huge quantities of waste cooking oil: China generates 826 million gallons, the United States generates 3 million gallons, and other countries produce even more (*6*). Disposal of this waste cooking oil is a primary concern because it may lead to ecological, environmental and municipal problems. In addition, WCO might tax sewerage lines to coagulate and block sewers if it is not properly discharged (*7*). Moreover, it will increase the organic load on the sewer system and create operational problems(*8*). Therefore, recycling of WCO in asphalt binder materials can be a source of proper conversion of waste materials to sustainable materials.

A number of studies have been conducted worldwide in the reuse of WCO due to its consistent performance as a potential waste material to rejuvenate the asphalt binders (*9–18*). Zargar found (*19*) that using 3-4% of WCO can increase the penetration value and resemble original asphalt. Similarly, Asli (*20*) studied the physical properties of WCO as a rejuvenator with RAP materials and suggests that within 25% RAP can be used without compromising the performance of pavement mixtures while using a rejuvenating agent in the mixture. Another study was conducted in the USA by Wen (*21*) and found that the addition of WCO based binder increases low-temperature resistance and moisture susceptibility. However, the study noted that the resistance to fatigue cracking, rutting, and stiffness of the mixture, decreased as WCO based binder was added in the mixture. Contrary to a study conducted by Wen, significant fatigue cracking resistance was recorded by Maharaj (*15*) and concluded that the fatigue resistance of the mixture increased as WCO was added.

Most of the studies on this topic conducted in the past comprised only basic and rheological tests such as penetration, softening point, dynamic shear rheometer (DSR), bending beam rheometer (BBR), and recommended that WCO can be utilized in asphalt pavement construction. While these tests provide information on the overall performance of the asphaltic materials, they are not designed to provide information on their fundamental properties or to capture the interaction that occurs between WCO and aged or virgin asphalt.

During the blending of WCO with asphalt, the interaction occurs at an atomic/nanoscale level, and it is recommended to understand the behavior of WCO rejuvenated asphalt at the microscopic level. When this research was conducted, there was insufficient research to understand the performance of WCO at a fundamental level. Recently a new concept has been introduced on pavement construction in the Netherlands that uses a microcapsule containing WCO (microWCOs) as a rejuvenator. Schlangen along with his team (*22*) developed an encapsulation system (1.60mm medium size) to use in porous asphalt pavement. The test results show higher tensile resistance of capsules and better skid resistance after eliminating the use of direct oil in the pavement. Correspondingly in China, Su (*23*) used microWCOs, fabricated by a shell membrane using a prepolymer of methanol melamine formaldehyde (MMF). The study reported that microWCOs could be penetrated in an aged binder and survive in melting bitumen, showing thermal stability and survival during repeated loading tests. So, from the evaluation of previous studies, it is noted that WCO may not be used as a full replacement of the binder, but maybe a satisfying rejuvenator to use in flexible pavement construction.

The primary objective of this study is to develop a quantitative understanding of the performance of WCO as a rejuvenating agent for the aged binder. In addition, this research also attempts to fill an existing gap in the literature concerning the interaction effects of WCO and other asphalt modifiers. To realize these goals, scientific laboratory investigation was conducted after collecting WCO samples from restaurants, and waste management company. In the laboratory investigation, rheological properties of rejuvenated asphalt were characterized using Rotational Viscometer (RV), and Dynamic Shear Rheometer (DSR). Besides, chemical characteristics and the molecular properties of WCO as well as for the WCO rejuvenated binder were evaluated by some advanced tests such as Gas Chromatography-Mass Spectroscopy (GC-MS) to identify the chemical composition of WCO, Fourier Transformed Infrared Spectroscopy (FTIR) for obtaining function group information, Atomic Force Microscope (AFM) for obtaining micrographs of the specimens surface profile, and Surface Free Energy (SFE) to evaluate the contact angle and adhesion characteristics of WCO rejuvenated asphalt.

2. Material Collection and Experimental Design

2.1. Asphalt Binder

The base binder used in this study is PG 58-28, which is generally used for city of St. John's pavement construction. The asphalt was collected from Advanced Roads and Transportation Engineering Lab (ARTEL), which was supplied by Bitumar USA, Inc. Later this virgin asphalt was being short-term aged by TFOT method, and the prepared aged binder was used as a control binder for this study.

2.2. Waste Cooking Oil (WCO)

WCO was selected as the rejuvenator for this study. Waste cooking oil was collected from two different sources (NJs Kitchen Restaurant and Eco Oil Limited). The collected oil samples consisted of lots of fried fragments as can be seen in Figure 1, which were separated using standard chemical process. To remove coarser and unwanted particles from oil, a fine screener was used for filtration. Based on the purity and appearance of the oil after filtering, the oil from the second source was used for the total experimental work. The chemical properties of WCO will be discussed in the later part of this report.

2.3. Experimental Scheme

The raw oil samples were filtered and underwent gas chromatography and mass spectroscopy (GC-MS) techniques to detect free fatty acid and fatty acid methyl esters (FAME) contents in the oil. This test provides good insight regarding the chemical composition of the rejuvenator. Based on the insight fatty acid contents, the transesterification process was applied to reduce the acid contents from the raw WCO.

Figure 1 Raw WCO

The rejuvenated asphalt was prepared by adding 3%, 6% and 9% of both treated and untreated WCO based on the weight of the binder. To understand the rheological properties of aged and WCO rejuvenated asphalt sample, rotational viscometer (RV) was employed. Later, Fourier Transform Infrared Spectroscopy (FTIR) was also conducted to understand the functional groups of the aged and oil rejuvenated asphalt binder.

3. Chemical Properties of WCO

The chemical properties of waste cooking oil (WCO) are the fundamental characteristics that dominate the behavior of asphalt. The quality of WCO is determined by the quantity of free fatty acid (FFA) exists in any WCO. FFA is produced during frying activities by the hydrolysis process as the oil is continuously heated to high temperatures with the presence of moisture and air content that creates several degradation processes (*24*). The quantity of FFA depends on the degradation process, operation temperature during frying activities, as well as the presence of impurities in WCO(*10*, *25*). The presence of FFA weakens the adhesion with bitumen. Besides, it reduces the binder properties which have an adverse effect on pavement mixture performance. There are several analytical methods to identify the components in oil and fats, like high-performance liquid chromatography-mass spectrometry (HPLC-MS), nuclear magnetic resonance (NMR), high-performance size exclusion chromatography (HPSEC), and gas chromatography-mass spectrometry (GC-MS)(*26*). Among them, GC-MS is a simple, fast, reliable and widely used technique to quantify the compositions of fats and oil. To execute GC-MS analysis, direct injection of the sample into the equipment system is not possible. This is why it requires a proper sample preparation and GC-MS operation method.

3.1. Sample Preparation

This experimental study was performed to identify and quantify the fatty acids and fatty acid methyl esters (FAME) in WCO. This study used methylation procedure for GC-MS analysis, shown in Figure 2. The sample was methyl esterified by potassium hydroxide/methanol (KOH/MeOH) method as per ISO 12966-2:2017 (*27*). In the derivatisation process, 0.03g sample was mixed with 1mL 0.5 mol L^{-1} KOH/MeOH solution along with 1 mL n-hexane. The combined solution was vortexed for 30 mins and then centrifuged. To make the solution acidic and neutralized, a sufficient amount of hydrochloric acid (HCl) was added and tested with a pH kit. After that, the upper n-hexane layer was collected from the separated two layers of solution for further injection in the GC-MS system.

3.2. GC-MS Operational Technique

An Agilent DB-5 MS (Agilent technology, USA) was employed to analyze the FAME in WCO. A capillary column of 30m in length having an internal diameter of 0.250mm and film thickness of 0.25μm were used. Table 1 lists the conditions of GC-MS operation.

3.3. GC-MS Analysis of WCO

The GC-MS analysis was performed for the WCO on an Agilent DB-5 MS system (Figure 3) with NIST 08 spectral library. The retention time and the area percentages are recorded in Table 2. As

WCO is a complex mixture, there were over 30 peaks in the results. Only eight peaks were selected based on the minimum area of 5% of the largest peak.

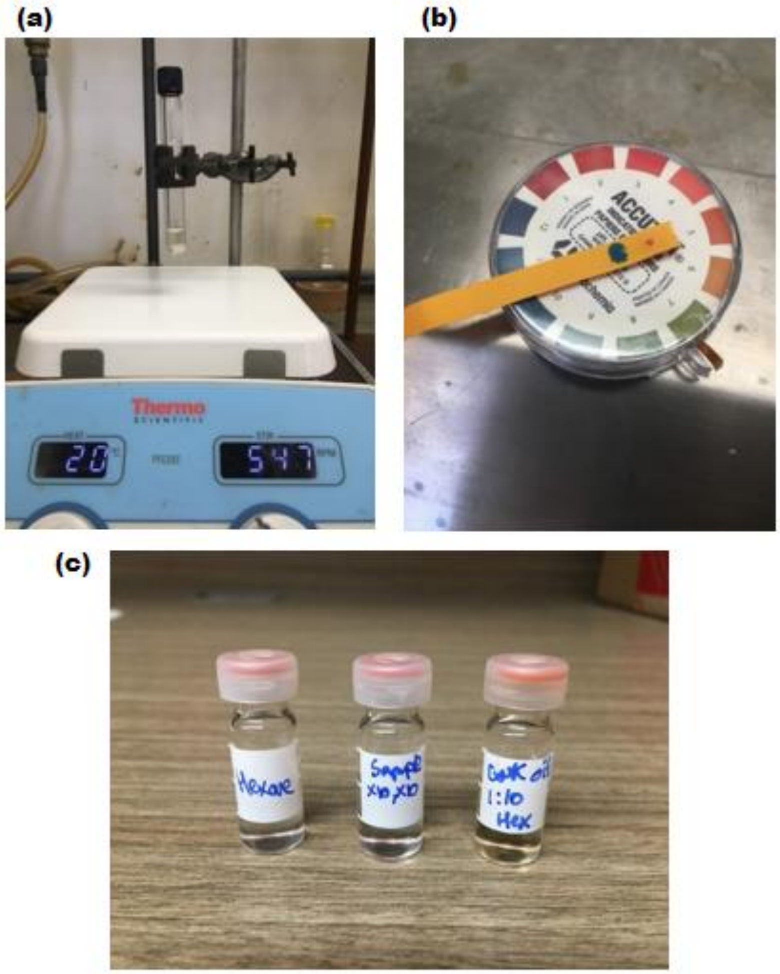


Figure 2 Sample preparation for GC-MS analysis (a) Vortexed solution (b) pH test, and (c) Prepared solution and solvent ready for injection into GC

Figure 3 An Agilent DB-5 MS system

Table 1 GC-MS Instrument Operation Parameters for WCO

Instrument	Agilent DB-5 MS			
Inlet				
Injection type	Split mode			
Injection temperature	250 ºC			
Injection volume	$1\mu L$			
Split ratio	50:1			
Carrier gas	Helium			
Flow rate	1 mL/min			
Column head pressure	12.77 psi			
Oven				
Oven Program	ºC/min	Next ºC	Hold	Runtime
	-	140	5	5
	2.50	240	10	55
Mass Spectrometer (MS)				
Auxiliary temperature	230 ºC			
Solvent delay	3 mins			
Mode	Scan			
Quadrupole temperature	150 ºC			
Scan mode range m/z	50-550 u			

Table 2 Chemical Composition of WCO from GC-MS Analysis

Peak #	Retention time (min)	Molecule	Synonym	Area Percent (%)	Molecular Weight (g/mol)
1	22.334	9-Hexadecenoic acid, methyl ester, (Z)	Palmitoleic acid	0.27	268
2	23.243	Hexadecanoic acid, methyl ester	Palmitic acid	5.42	270
3	29.37	9,12- Octadecadienoic acid (Z,Z)-,methyl ester	Linoleic acid	19.54	294
4	29.867	9-Octadecenoic acid (Z), methyl ester	Oleic acid	68.51	296
5	30.616	Octadecanoic acid, methyl ester	Stearic Acid	2.91	298
6	36.48	Cis-11-Eicosenoic acid, methyl ester	-	1.97	324
7	37.434	Eicosanoic acid, methyl ester	Eicosanoic acid	0.95	326
8	43.818	Docosanoic acid, methyl ester	Myristic acid	0.43	354

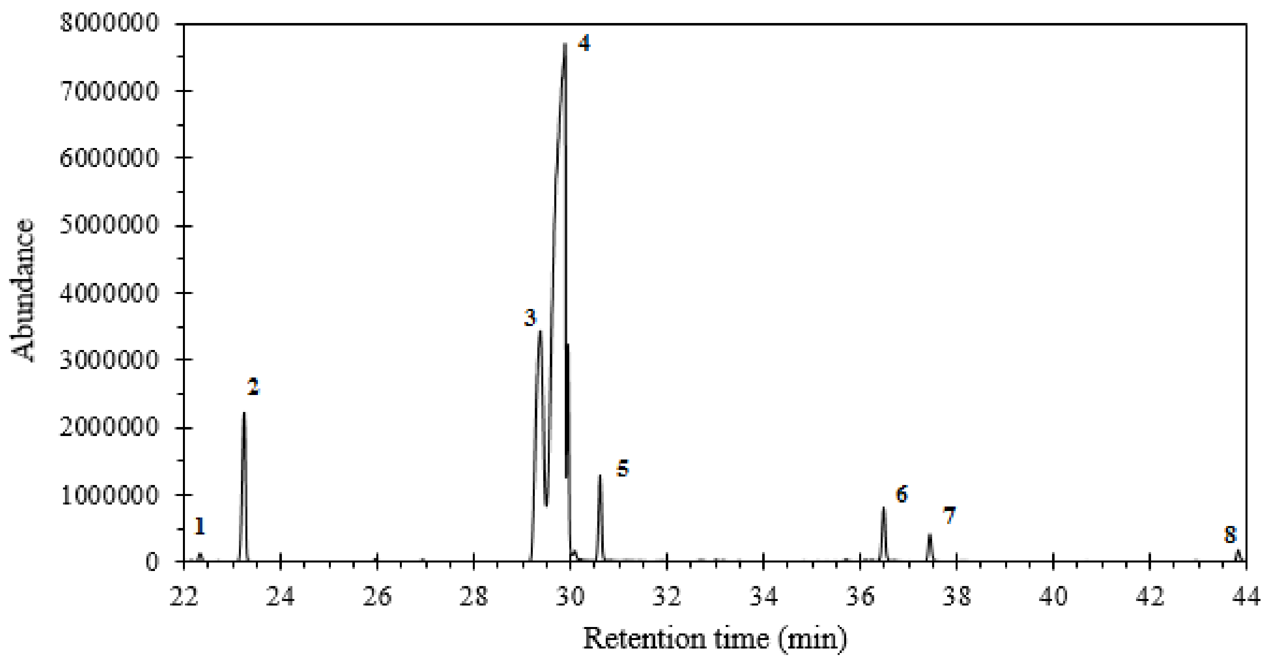
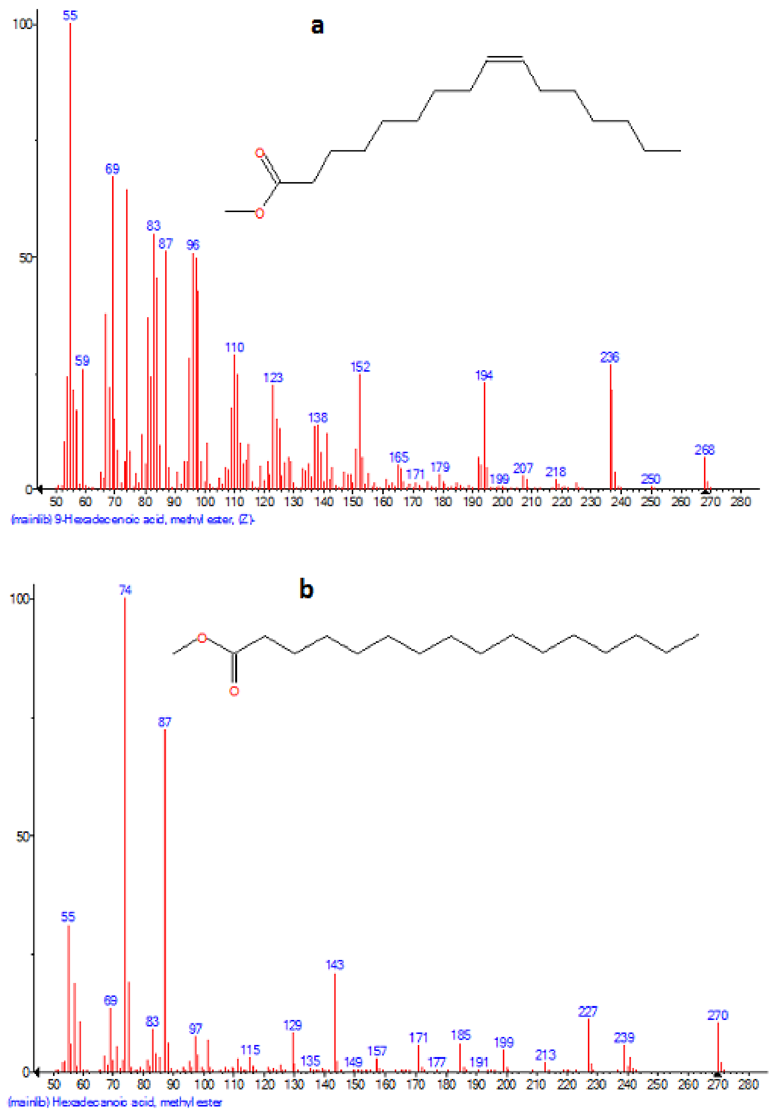
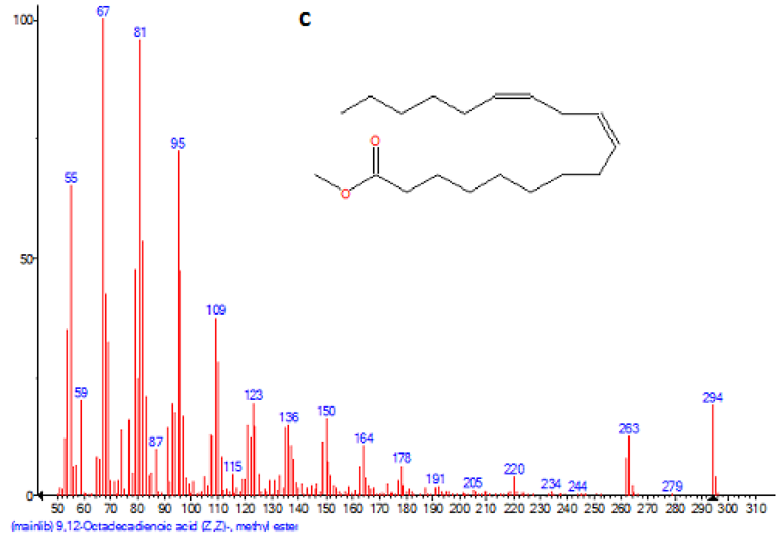


Figure 4 Chromatogram of WCO

Figure 4 shows the chromatograms of the WCO sample. All the main components were identified in the chromatograms and also separated from each other. It is also mentioned that, the solvent n-hexane has not shown in chromatograms for clarity. From the chromatograms, it is clear that all the peaks belong to the long chained C16-C18 fatty acid methyl esters (FAME)(*28*). The molecular weight of all the FAME ranges from 260-360 g/mol which is much lower than asphalt (700 g/mol). Oleic acid and Linoleic acid appears at the retention time of 29.86 min and 29.37 min having the highest area concentration of 68.5% and 19.54% respectively. As fatty acid has been converted into FAME by the methylation process, the three main components were found in WCO: Oleic acid (68.51%), Linoleic acid (19.54%), and Palmitic acid (5.42%). The mass spectrums of all eight components along with their molecular structures has been represented in Figure 5.

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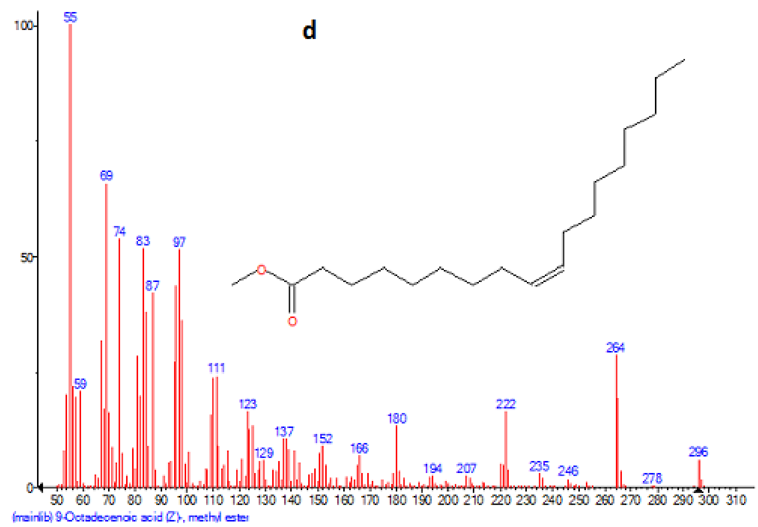
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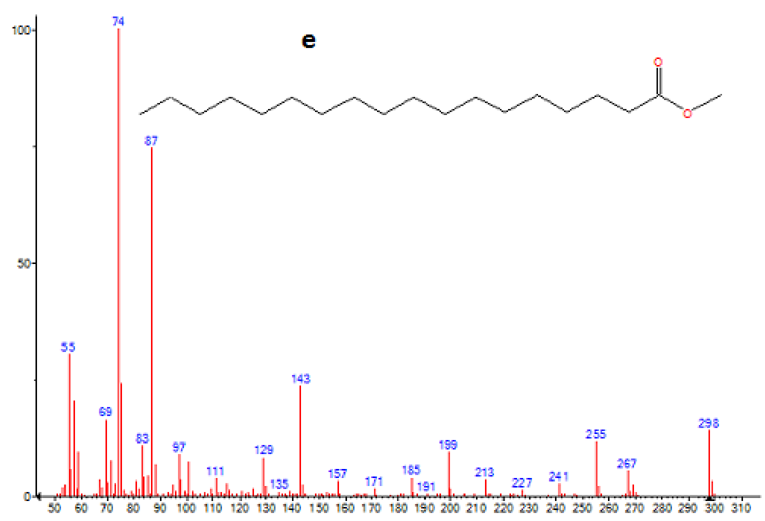
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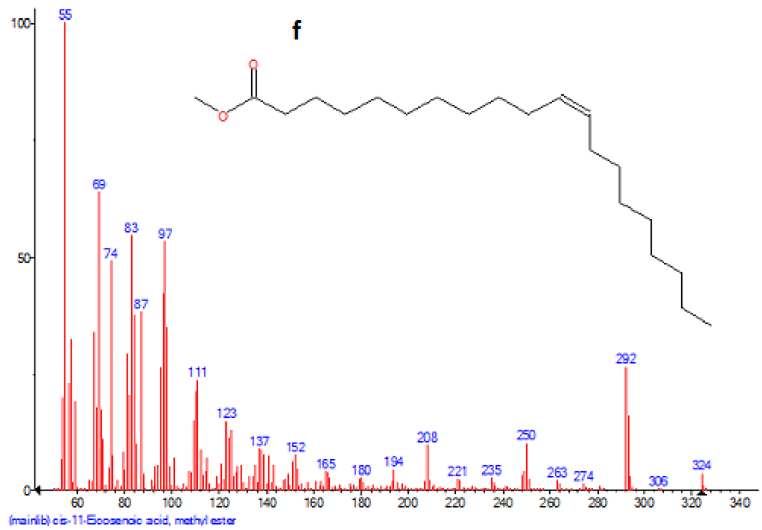
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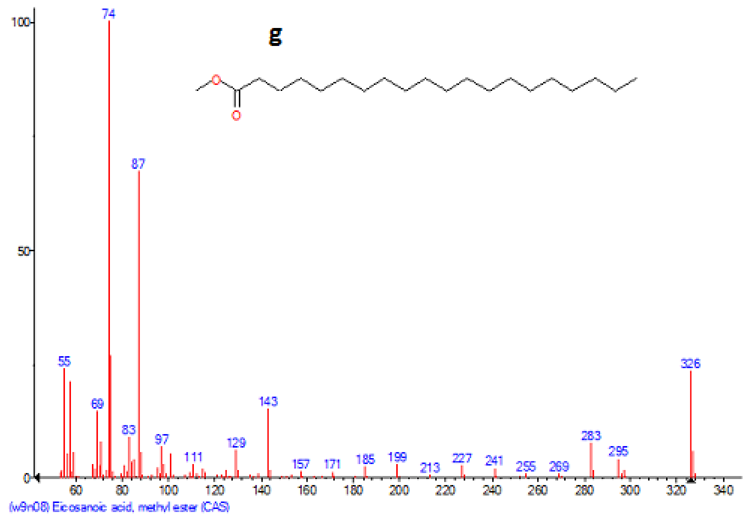
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(w9n08) Eicosanoic acid, methyl ester (CAS)

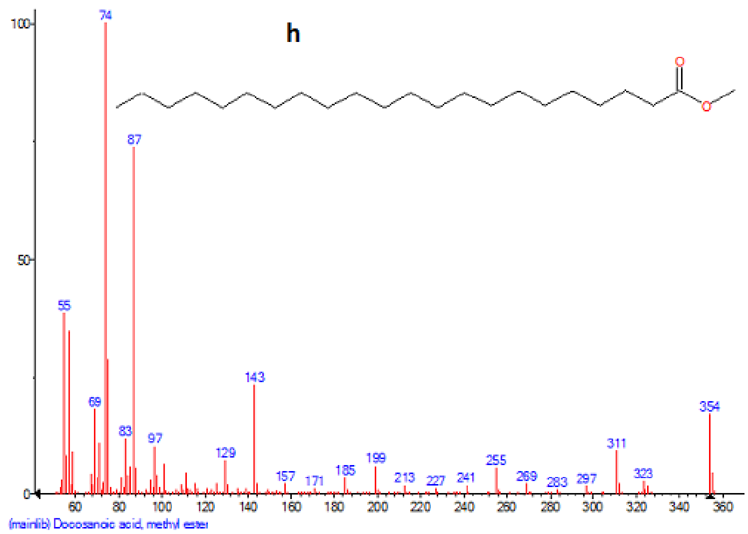


Figure 5 Images of all the acid components from the mass spectrometer: (a) Palmitoleic acid, (b) Palmitic acid, (c) Linoleic acid, (d) Oleic acid, (e) Stearic Acid, (f) Methyl cis-11-eicosenoate, (g) Eicosanoic acid, and (h) Myristic acid

Molecular structure from Figure 5 exhibits that all the molecules have both polar ($-CH_2-$) and non-polar (-COO-) ends, which denotes that molecules are hydrophilic and have a strong affinity to water. This affinity has a harmful effect on the overall moisture susceptibility of asphalt when mixed with WCO. Besides, this FAME might have negative effects on their rheological properties (*29*). It can be concluded that the reduction of these fatty acid content is required for better performance of WCO rejuvenated asphalt.

4. Preparation of Samples

4.1. Modification of WCO

WCO is generally contains high free fatty acid contents and the percentages of FFA might vary over sources. The generation of FFA depends upon the longer duration of frying activities and also with the type of food habits across the world. The acid value test is an indicator to determine the free fatty acid content in fats and oil. With the difference with the source of collected WCO, the acid value also differs. Typically, the acid value varies from 2%-7% for WCO sample (*29*). The lower the acid value, the higher the performance of rheological properties (*30*). The acid value test is conducted according to ASTM D5555 (*31*),and based on the acid value (Table 3) further treatment process is selected. From the previous literature, the authors have recommended for transesterification process for the treatment of WCO.

4.1.1. Transesterification Process

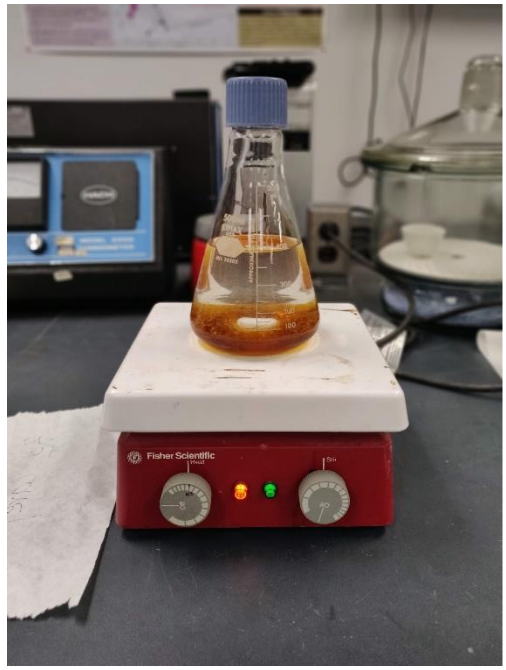
Transesterification is a common method used to produce bio-diesel using alkali catalysts. This process included some chemical reactions of WCO with methanol and NaOH. Prior to executing the transesterification process, several parameters should be selected (i.e., total reaction time, volume of methanol to oil, and the concentration of NaOH). These parameters have significant impacts on the final products and the proper conversion of WCO.

Table 3 Acid Value of treated and untreated WCO

Sample	Volume of KOH (mL)	% Free Fatty Acid (based on Oleic acid %)	Acid value (mL/g)
Untreated WCO	0.70	2.74	5.45
Treated WCO	0.25	0.97	1.95

Based on the study of Leung et al. (*32*) the optimum ratio of methanol to oil is 7:1 with the concentration of 1.1% NaOH of the volume of oil and the reaction time of 20 min when the temperature achieved at 60 ºC. In a simplified procedure, a total of 100 mL oil, 700 mL methanol and 1.1 mL NaOH was being mixed properly. Later, this solution was placed on the heater, and a magnetic stirring bar was inserted into the solution to make a homogeneous mix. When the temperature reached to 60 ºC, the reaction started, and the solution was heated for the next 20 min. The solution was kept overnight to allow the two phases to become separated. The upper phase is treated WCO (esters) and the concentrated lower phase was glycerol. The upper phase was light yellow in color, whereas the lower phase was dark brown in color as shown in Figure 6. Also, the treated and untreated sample is presented in Figure 7.

(a)



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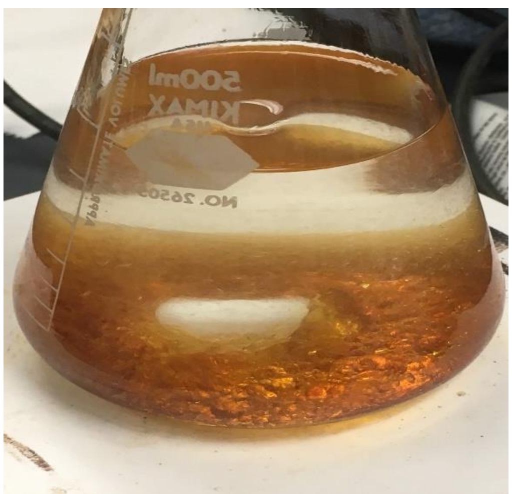

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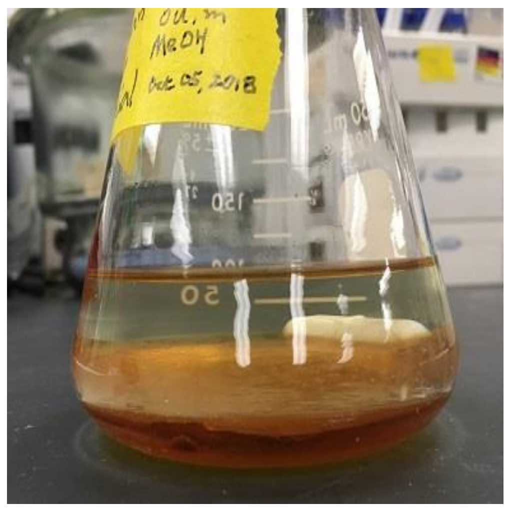

(d)

Figure 6 Transesterification process (a) mixed solution of oil, methanol, and NaOH, (b) prepared solution on hot plate, (c) beaker equipped with magnetic stirrer and the chemical reaction, and (d) separated two distinct phases after 24 hours.

Figure 7 Untreated WCO (left) and Treated WCO (right)

4.2. Asphalt Binder Aging

Asphalt binder experiences an enormous environmental impact after pavement construction (*33*). These environmental impacts include hot air, high temperature, UV radiation, and many unknown chemical compounds. During their interaction, asphalt started to lose its rheological and physical properties. To experience these practical conditions in the laboratory, two aging methods are generally employed. Rolling Thin Film Oven (RTFO) and Thin Film Oven (TFO) tests represent short term aging, and Pressure Aging Vessel (PAV) test represents the long term aging condition. This study was limited within the short term aging using TFOT method as per ASTM D1754 (*34*). In this method, the neat liquid asphalt (PG58-28) undergoes a constant heat of 163ºC for 5 hours to age the asphalt. During this aging process, asphalt started to loses its mass due to oxidation and high temperature as shown in Table 4. For this study, this prepared aged asphalt has been selected as the base asphalt.

4.3. Blending Rejuvenators and Asphalt Binders

Rejuvenated asphalt binder was prepared by mixing TFOT aged asphalt binder with two types of oil: 1) Untreated WCO, and 2) Treated WCO. First, the aged asphalt was heated to make it fluid enough to mix it with oil. TFOT aged asphalt was mixed with the different application rate of untreated and treated WCO, namely 3%, 6%, and 9% by the weight of base asphalt. The percentages of mixed waste oil were determined from the literature review. The blending process was conducted manually with a glass stirrer for 30 mins at 100ºC. Both the rejuvenators were liquid and had low viscosity, that why this blending time was selected to achieve a homogeneous mix. Therefore, the prepared samples were used for further experimental analysis. An overview of the total preparation procedure has been shown in Figure 8.

Table 4 Mass of Change after TFOT aging

Sample No	Beaker weight	Asphalt Wt. (Before test)	Asphalt + Beaker Wt. (After test)	Asphalt Wt. (After test)	Mass change	Remarks
1	11.2	32.2	43.3	32.1	-0.311	Loss
2	11.9	30.6	42.4	30.5	-0.327	Loss
3	9.5	29.9	39.2	29.7	-0.669	Loss
4	9.6	31.5	41.3	31.7	0.635	Gain
5	10.2	30.0	40.1	29.9	-0.333	Loss

5. Investigation of WCO modified binder using rheological testing

5.1. Rotational Viscosity test

The Superpave mix design requirements have given more emphasis on using different types of modifiers as they show better performance (*35*, *36*). During pavement construction, one of the important issues is selecting mixing and compaction temperature to achieve a better field performance of asphalt (*37*). The selection of mixing and compaction temperature is vital, and inaccurate approximation of temperature may cause degradation of binder property and may also create premature failure of pavement (*38*, *39*).

Generally, the conventional way of accessing the mixing and compaction temperature is based on the viscosity property of that binder. Viscosity is a property that is used to characterize the shear resistance of binder with an external force and a specified rotation using a viscometer. This study used a Brookfield Rheometer along with a Thermosel Temperature Controller, shown in Figure 9 (produced by Brookfield Engineering Laboratories Inc, Middleboro, MA, USA) to execute the experimental work. The speed was fixed to 20 rpm with the density of asphalt 1.006 g/cm^3. Based on the efficiency of equipment, the QC limit was selected between 100 ºC-180±1 ºC.

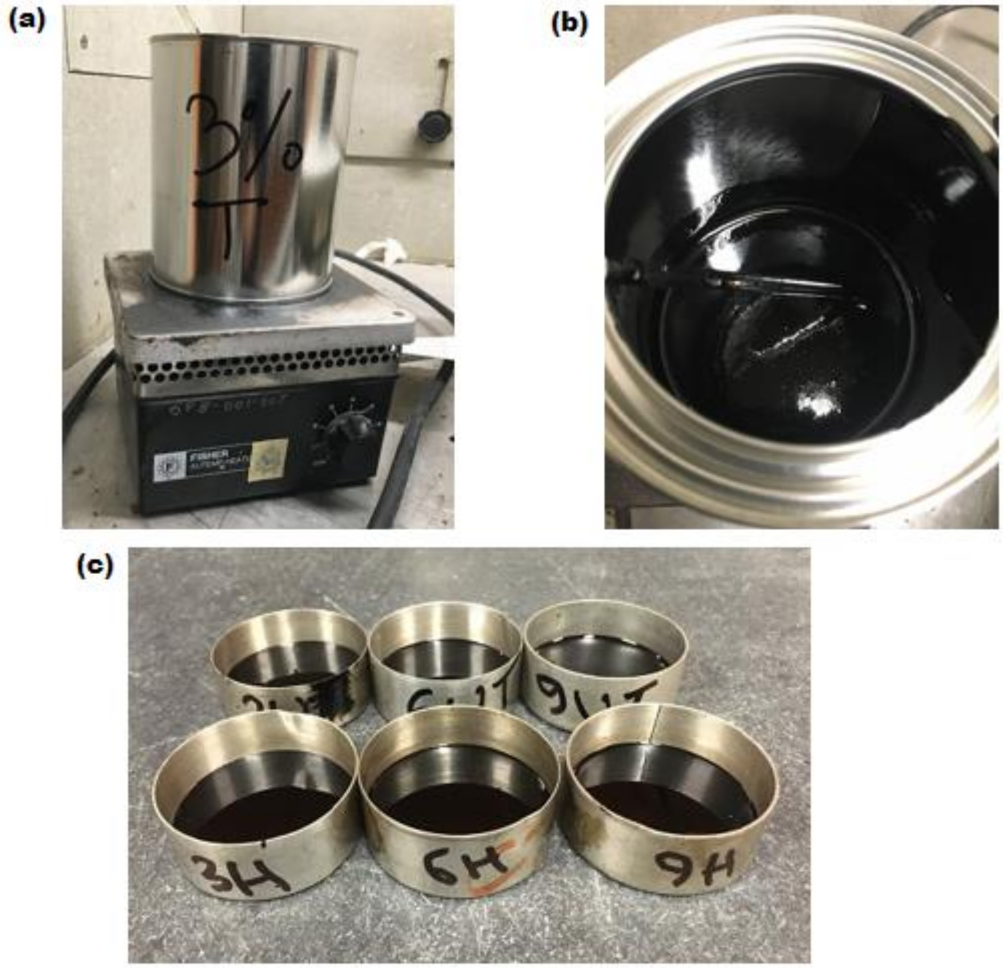

Figure 8 Preparation of Rejuvenated asphalt binder (a) Heating of aged asphalt, (b) Manual Mixing with a glass rod, and (c) Prepared sample after the mix

Figure 9 Brookfield Rheometer with Thermosel (left) and Programmable Temperature Controller (right)

5.2. Analysis and Discussion

Rotational viscosity test results of WCO rejuvenated asphalt (treated and untreated) at the range 110 ºC- 175 ºC has been illustrated in Figure 10. Based on the results demonstrated in the figure, a decreasing trend was observed for both treated and untreated WCO rejuvenated asphalt sample. However, this trend of decreasing viscosity is more severe for the untreated sample compared to the treated sample. It is also noted that the change of their viscosity was more comparative (850 cP-1600 cP) at the initial stage but ended with almost the same viscosity of 60cP-70cP at 175 ºC.

Figure 11 exhibits the changed of the viscosity before and after the rejuvenation at 135 ºC and indicates the restoration property of treated and untreated WCO rejuvenated asphalt. The viscosity value of unaged PG58-28 asphalt was recorded 380 cP which is very close to 3% untreated WCO sample. This result proves that after rejuvenation with WCO, the aged asphalt having a viscosity of 508 cP can restore the viscosity of virgin asphalt. Correspondingly, 3% treated WCO rejuvenated asphalt shows almost the identical viscosity with the RTFO aged PG58-28 asphalt, which indicates that the improvement of WCO quality can increase the flow resistance and internal friction than unaged PG58-28 binder. With the addition of more quantity of treated WCO, viscosity follows a decreasing trend and always exhibits good internal resistance than unaged asphalt. A similar trend was also observed when more percentages of untreated WCO were used, and in that case, even lower viscosity than unaged sample was obtained.

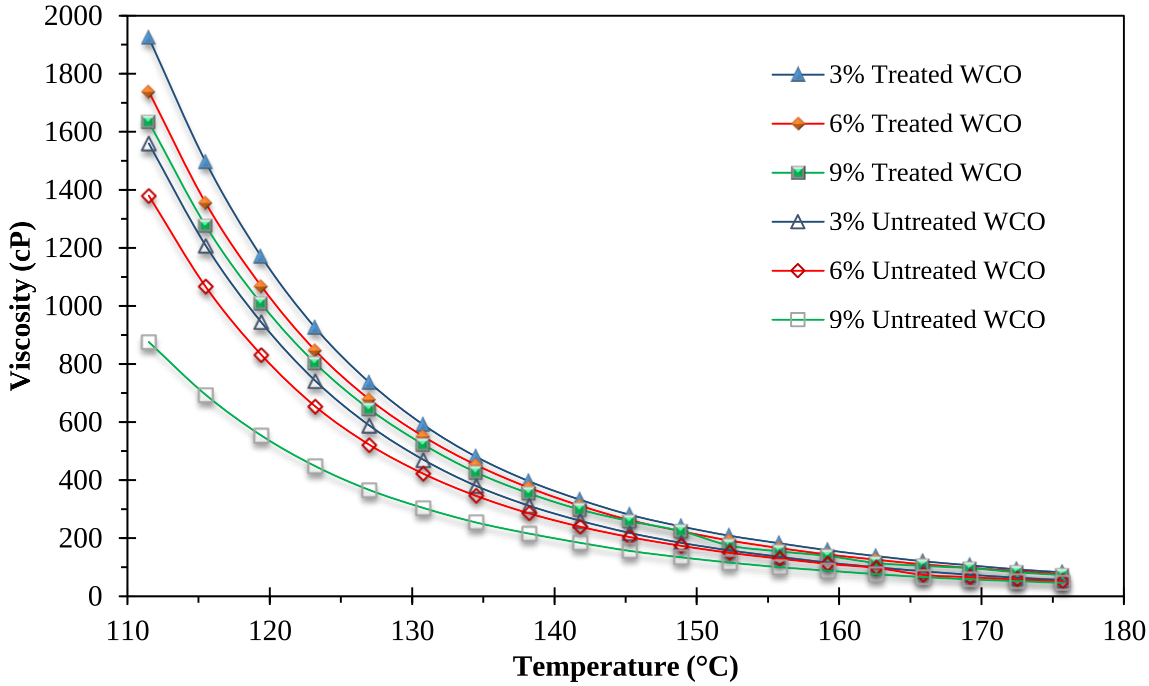

Figure 10 Rotational Viscosity test value for treated and untreated WCO rejuvenated asphalt

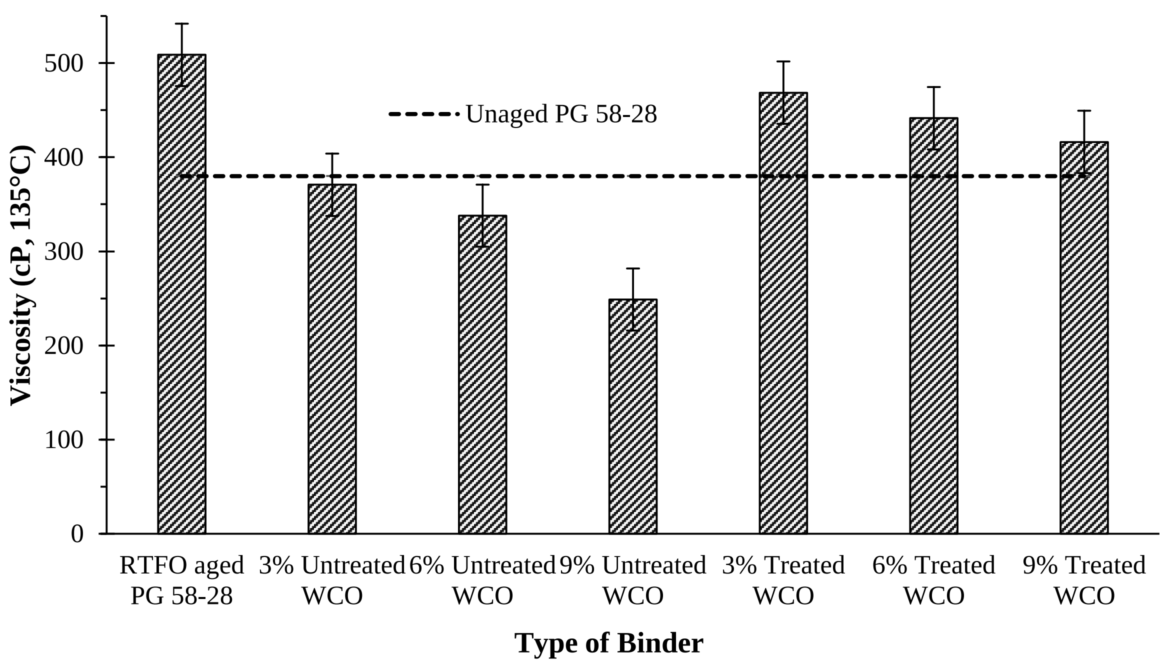

Figure 11 Change of Viscosity for virgin, RTFO aged and WCO rejuvenated asphalt at 135 ºC

Generally, WCO was selected based on their acid value, and the WCO with lower acid value or low viscosity is preferred for asphalt rejuvenation. Also from the economic perspective, the lower viscosity can reduce the mixing and compaction temperature of the mix. The reduced mixing and compaction temperature is favorable in the construction site and also for saving cost. Although the lower viscosity can be achieved using an excessive quantity of WCO, then it might be a matter of poor serviceability. The lower the serviceability, the material will be softer and susceptible to rutting. Compared to untreated WCO, the treated WCO can be used to achieve higher internal resistance as well as for higher viscosity. The higher viscosity is also related to the high adhesive performance of the mixture. This study concludes that using treated WCO might improve the flow resistance and internal friction of asphalt. The better chemical composition will also be achieved using treated WCO compared to untreated WCO and might increase the rutting resistance of the mixture. Based on this study, it is recommended to use lower acid valued WCO having a reasonable range of viscosity.

6. Effect of WCO on Asphalt Oxidative Potential

Fourier Transform Infrared Spectroscopy (FTIR) was used to analyze the chemical functional groups of asphalt. FTIR is the only analytical method which provides ambient temperature operation and to directly monitor the vibrations of the functional groups simultaneously which characterize the molecular structure and govern the course of chemical reactions (*40*). In principle, FTIR also provides continuous (near real-time) and low maintenance operation compared to gas chromatography and mass spectroscopy.

6.1. Sample Preparation and FTIR Operational Techniques

A Bruker series FTIR (presented in Figure 12) was used to analyze the functional groups of asphalt. This machine is equipped with a diamond ATR (Attenuated Total Reflection) that allows measuring the changes that occur in the IR beam. ATR technique helps to examine the sample directly either in a solid or liquid state without any special sample preparation techniques. Based on the previous experimental analysis, the scan range was selected from $400cm^{-1}$ to $4000cm^{-1}$(*40*). The final detection of functional groups in the sample were detected after completing 36 scans to reduce any error.

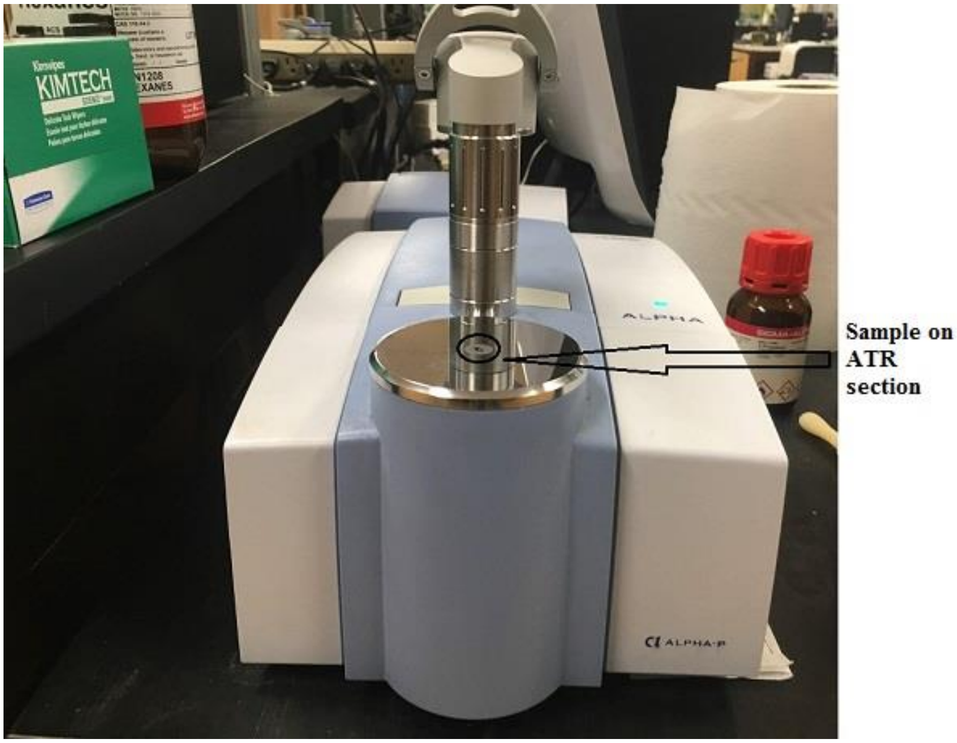

Figure 12 A Bruker series FTIR Equipment

The sample preparation technique is straightforward compared to other methods. The sample which has been prepared after blending with WCO can be used for this test. Firstly, the spatula was heated at high temperature to melt the asphalt sample when it can come in contact with asphalt. The spatula was inserted at a required depth of the sample can to take the sample. To avoid any errors, sample was not taken from the top surface because this layer might be contaminated with dust or other unwanted particles. After collecting a drop of sample, it was scratched smoothly on the ATR surface, and then the automated computed system started detecting the functional groups of the sample. For the next test, the scratched sample was removed using n-hexane which is highly soluble in asphalt.

6.2. Spectrum Analysis and Discussion

The functional groups of rejuvenated asphalt binder (before and after treatment of WCO) was analyzed by IR spectrum table (*41*, *42*) and represented in Figure 13 and Figure 14 respectively. Also, the typical spectrums of aged asphalt have been shown in Figure 13 and Figure 14. Based on the previous studies (36), the analysis was conducted in the region from 400 $cm^{-1}$to 4000 cm^{-1} to identify the corresponding peaks of the binder. Out of those bands, 1032 cm^{-1} and 1744

cm^{-1}correspond to sulfoxide (S=O), and carbonyl (C=O) respectively that reflects the aging and rejuvenating degree of asphalt (*43*). The carbonyl peak at 1744 cm^{-1} belongs to the ester carbonyl functional group which exhibit the existence of cooking oil in rejuvenated asphalt which is not found in aged asphalt and a very negligible amount in treated WCO sample. The intensity of C=O bond is 0.053, 0.091, and 0.108 respectively for 3%, 6% and 9% of untreated WCO sample. Whereas, this peak intensity decreased gradually when treated WCO was used as the quality of the oil increased. Also, this C=O bond is a saturated aliph and it is, responsible for making the binder softer which is more prone to rutting (*29*). Based on that, it is a clear indication that the quality of WCO has a notable influence on the chemical composition of rejuvenated asphalt that reflects the overall performance of the mix.

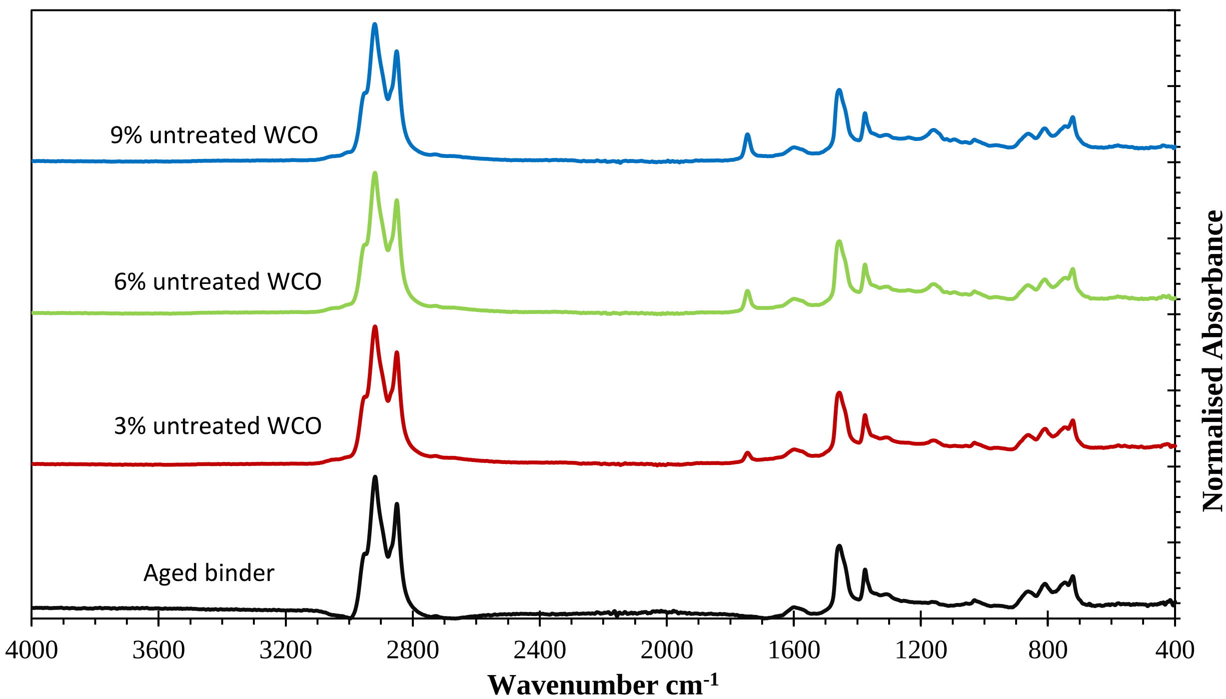

Figure 13 Normalised FTIR spectra of aged and untreated WCO rejuvenated asphalt binders

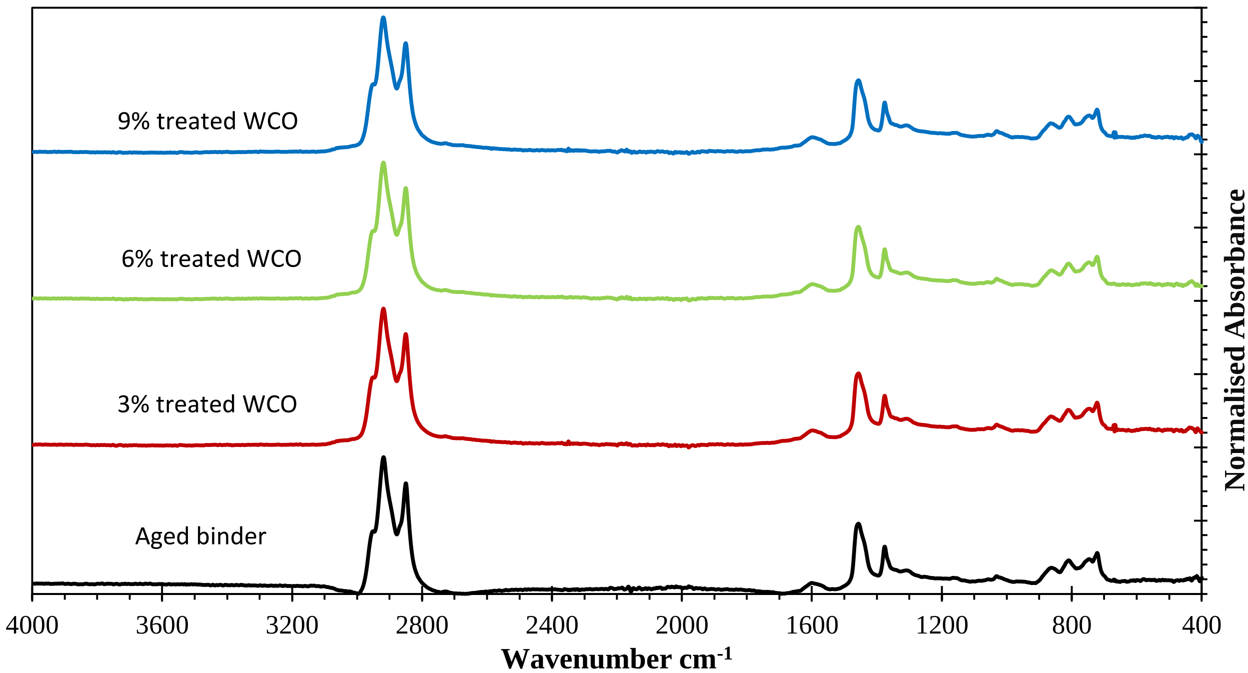

Figure 14 Normalised FTIR spectra of aged and treated WCO rejuvenated asphalt binders

For the treated, untreated and aged sample, the highest peak was detected at 2921 $cm^{-1}$and 2851.91 cm^{-1} that belongs to the Sp^3 C-H methyl group. For both type of WCO, the major difference was their intensity. The intensity decreased with the increase of oil percentages and for treated WCO, the higher intensity was recorded than untreated WCO. Another Sp^3 C-H and C=C (alkane) bond was detected at 1374 $cm^{-1}$and 725 cm^{-1}respectively. These peaks intensity was about same for three types of sample and does not have any influence. The presence of C=C aromatic bond was detected at 1452 $cm^{-1}$for all the samples which exhibits a strong bonding of the constituents. For aged asphalt the intensity was 0.283, whereas for treated and untreated sample, the intensity increase with the decrease of oil percentages. And treated sample shows better intensity like before.

To differentiate between the treated and untreated sample, C-O alcohol peak is the only deterministic functional group. The C-O bend was detected for untreated WCO sample at 1161.15 cm^{-1}wavelength with an intensity of 3% = 0.102, 6% = 0.119, and 9% = 0.127. However, this group was not present in treated and aged sample. This might be the reason of treatment of WCO and reduction of free fatty acid after trthe ansesterification process. There was another distinct peak of Sulfoxide (S=O) was found at 1032 cm^{-1} which is an identification of the only aged sample, and not present in unaged sample. This characteristics also matches with other previous studies worked with aged asphalt (*44*, *45*). The intensity of S=O peaks varies with the quality of the WCO used and it is higher for treated WCO followed by untreated WCO and aged sample. Therefore, the conclusion can be drawn from the FTIR spectrum analysis that the chemical constituents can be changed with the quality of WCO used. In addition, with the higher acid content in the WCO sample might soften the binder which is an indication of decreasing rutting resistance and the increase of moisture susceptibility of the asphalt mixture.

7. Conclusions

To reduce the dependency on neat asphalt and to make sustainable pavement, asphalt binder from RAP has been considered as an economical pavement construction material. Rejuvenators are commonly used to enhance the rheological and mechanical performance of RAP to extend its performance. This research aimed to understand the rejuvenating behavior of WCO in terms of their quality and its restoration of fundamental properties of virgin asphalt. From the experimental analysis, the following conclusions can be drawn for this study:

- Free fatty acid (FFA) was observed in WCO by GC-MS analysis, which enhances hydrophilic characteristic of asphalt binder and it is harmful for moisture susceptibility. Therefore, it is required to reduce the FFA content to improve the WCO quality.
- The improved quality of WCO after transesterification process influenced the rejuvenation behavior with aged asphalt, and higher quality WCO (lower acid value) can lead to better performance with aged asphalt.
- The improved quality of WCO enhanced the stiffness as well as the rejuvenating behavior of aged asphalt. Stiffness of the binder changed with the percentage of treated WCO added. The stiffness of the rejuvenated binder can be ranked as: treated WCO 3% > 6% > 9%.
- Rotational viscosity test found that the 3% untreated WCO can achieve the viscosity property of the virgin PG 58-28 binder, whereas 6% and 9% untreated WCO sample provided lower viscosity than control binder.
- Relatively high viscosity value was achieved for treated WCO as opposed to raw WCO. A higher viscosity was noticed when 3% treated WCO was added in aged asphalt, which followed a decreasing trend for the addition of 6% and 9% treated WCO. All the

percentages of treated WCO counterintuitively showed higher viscosity than virgin PG 58-28 binder.

- FTIR test results exhibited a higher rate of C=O stretch at 1744 cm^{-1} for untreated WCO, which is responsible for softening the binder and inducing rutting failure. Whereas, this stretch was very negligible for aged binder and a less amount for the treated WCO compared to untreated WCO, shows better rutting resistance. Therefore, quality improvement of WCO shows better composition of rejuvenation as well as the binder performance.

8. Future Works

Based on the experimental analysis and past studies, some recommendations are provided that could be done in the future:

- The province of Newfoundland and Labrador (NL) experiences severe weather conditions throughout the year. Therefore, roads in the province experience various distresses, for example rutting and cracking. Rutting and cracking resistance can be examined using DSR and BBR test. To understand in depth performance of pavement, these tests need to be done specially for a weather region like NL. For this project, the DSR test is in progress as a research collaboration with Yellow line Asphalt Products Ltd. in Ontario.

- The past studies related to WCO rejuvenated asphalt is on the rheological tests that provide only overall performance of binder. However, to access the properties at the fundamental level, the interaction should be determined at the microstructure level that required some advanced testing like AFM. AFM is capable of acquiring micro-mechanical information through surface topography at micro-level. With the collaboration of the Department of Physics of MUN, the test is in progress for this project.

- Due to weather condition at NL, there is rain or snowfall throughout the year which is one of the main reason for moisture damage and stripping between binder and aggregates. Due to stripping, surface distress and potholes are the common scenarios of pavement. To evaluate the moisture damage resistance of mix, and how the rejuvenators are performing to improve the cohesive energy of asphalt, as well as the adhesion with the aggregates needs to be determined through Surface Free Energy (SFE) test.

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Appendix A

Prior to starting the experimental analysis, a review article was prepared based on the existing literature of WCO rejuvenated asphalt in pavement construction. The prepared literature review paper has already been submitted to Construction and Building Materials, and the paper is now under review process. The overview of this review article is available in the following link.

Link to Overview of Review Paper: https://artel.engr.mun.ca/projects/application-of-waste-cooking-oil-in-construction-of-asphalt-pavements/

Appendix B

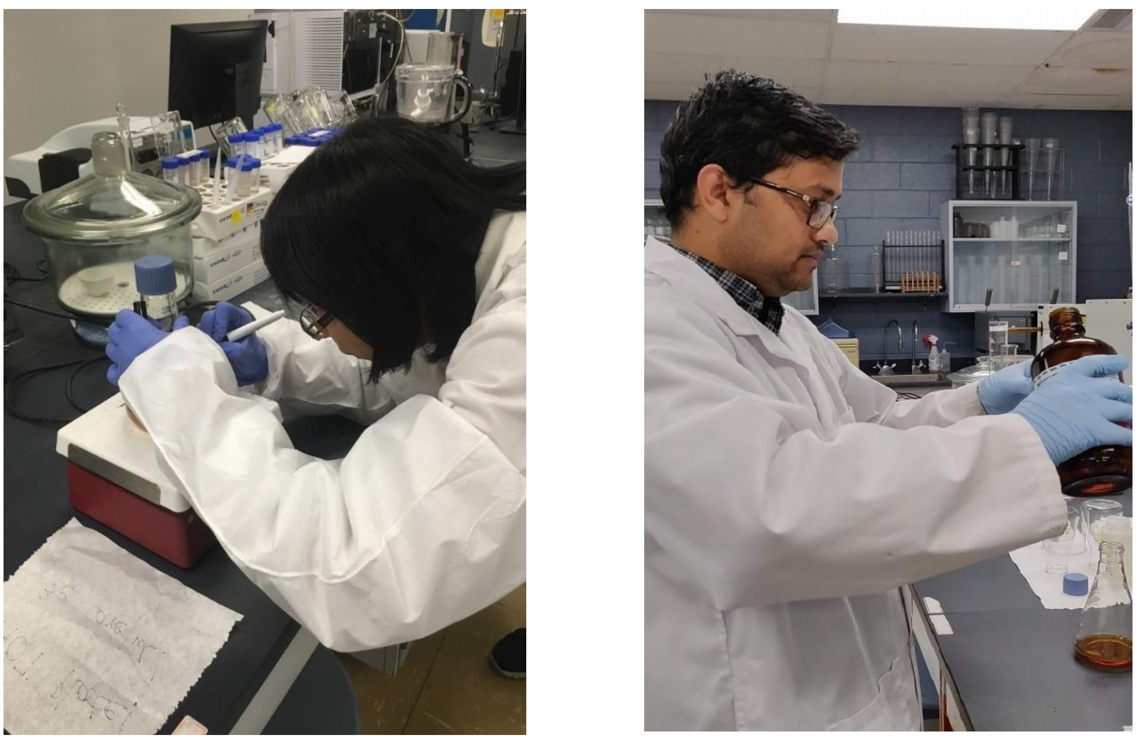

Figure 15 Modification of WCO at Environment Engineering Lab, MUN

Figure 16 Experimental work on Rotational Viscometer at Asphalt Lab in MUN

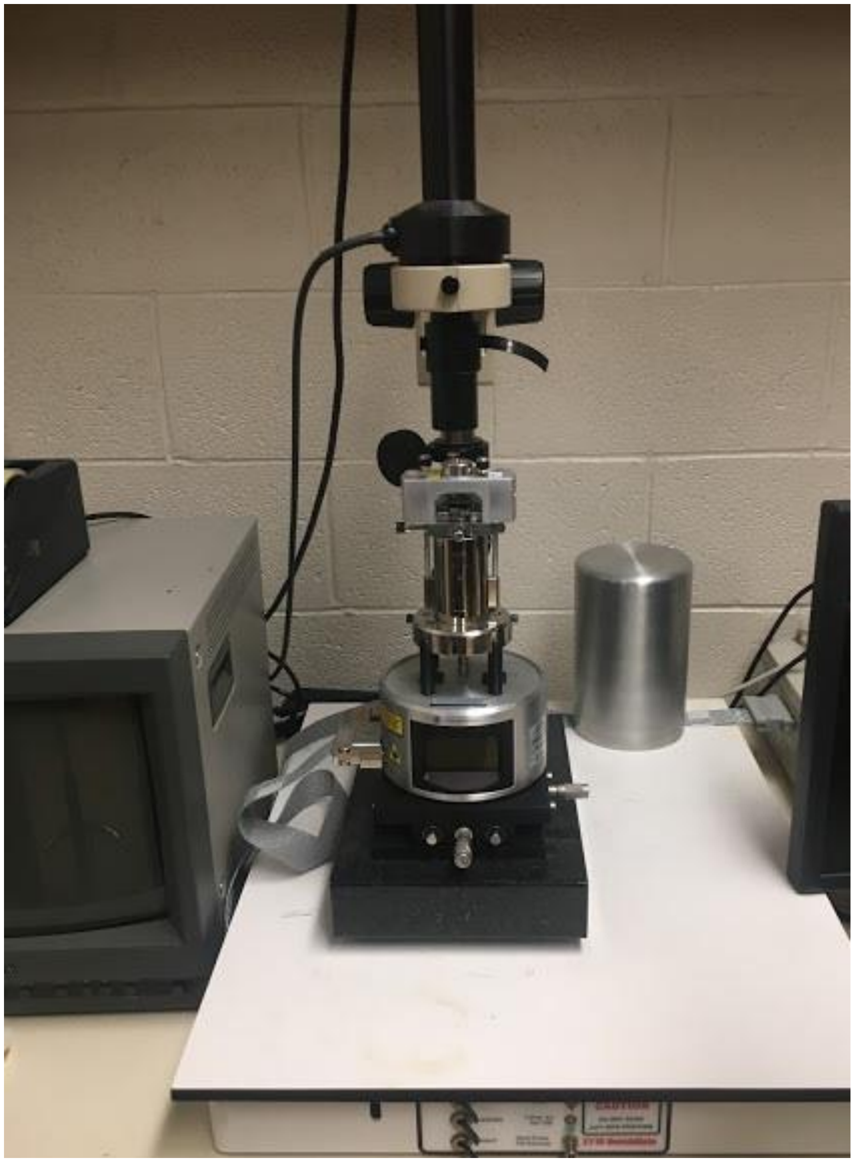

Figure 17 Micromechanical Test in Progress in Atomic Force Microscope at MUN